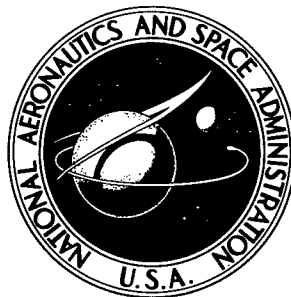


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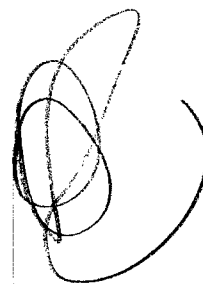
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**VAPORIZATION OF
TANTALUM-CARBIDE—HAFNIUM-CARBIDE
SOLID SOLUTIONS AT 2500° TO 3000° K**

*by Daniel L. Deadmore
Lewis Research Center
Cleveland, Ohio*

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SOLUTIONS AT 2500° TO 3000° K*

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SUMMARY

The vaporization rates in vacuum of hot-pressed hafnium carbide, tantalum carbide, and solid solutions of these two carbides in the temperature range of 2500° to 3000° K were determined by a Langmuir type method. The results show that a composition near 70 mole percent tantalum carbide · 30 mole percent hafnium carbide exhibits the lowest vaporization rate of any composition within this pseudobinary system. Variations in initial sample bulk density and vapor-specie condensation on the furnace wall have negligible effects on the measured vaporization rates. Preliminary information concerning the influence of time on the vaporization rate of selected compositions is discussed.

INTRODUCTION

The refractory carbides as a class have the highest melting temperatures of materials known today. As such, they are of interest as potential materials for applications that require high temperatures of operation. One such application is in the field of thermionic energy conversion. Thermionic parameters, for example, work function and emission flux, have been measured for some carbides (refs. 1 to 3) and suggest that these materials are useful emitters. A major liability of carbides for this application is the relatively high rate of vaporization. Excessive vaporization of an emitter material would lead to degradation of the critical cathode-anode spacing and the possibility of short circuiting the cell by condensation on electrical insulators.

The study reported herein was initiated to determine the vaporization characteristics of the binary carbide system tantalum carbide - hafnium carbide (TaC-HfC). This system was chosen for study because its components have the highest melting temperatures of the refractory carbides and low vaporization rates (refs. 4 to 7). The component carbides are soluble in all proportions (ref. 8). A composition within this solid-solution region, 80 mole percent TaC · 20 mole percent HfC, has been reported to have a melting temperature

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higher than either TaC or HfC (ref. 9). This presents the possibility that such a solid-solution composition might exhibit a vaporization rate lower than either component carbide.

In this study, the vaporization rates of TaC, HfC, and intermediate solid-solution compositions were determined in vacuum between 2500° and 3000° K by a Langmuir type method. A composition exhibiting minimal vaporization rate was found. The effect of vapor-specie condensation on vaporization rate was ascertained by making measurements in cold-wall (condensable vapor) and hot-wall (noncondensable vapor) furnaces. Preliminary experiments to determine the influence of time on the vaporization rate were also made.

EXPERIMENT

Materials and Sample Preparation

Table I shows the chemical and X-ray diffraction results for the commercially supplied starting materials. A formula for each material is given that includes the major metallic impurities. The $(\text{Ta}_{0.988}\text{Nb}_{0.011}\text{W}_{0.001})\text{C}_{0.932}$ composition will hereinafter be referred to as $\text{TaC}_{0.93}$; the $\text{HfC}_{0.982}$ will be re-

TABLE I. - CHEMICAL ANALYSIS AND X-RAY DIFFRACTION RESULTS OF STARTING MATERIALS^a

	TaC		HfC		80 TaC • 20 HfC	
	Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Analysis weight percent:						
Total C	5.96		6.20		5.85	
Free C	.11		.01		.03	
Combined C	5.87	6.22	6.19	6.30	5.82	6.23
Ta	---	93.78	---	---	74.23	75.21
Hf	---		93.72	93.70	18.92	18.56
W	.11		---		---	
Fe	---		<.005		.036	
Si	<.01		<.01		<.001	
Nb	.52		---		.32	
Ti	---		---		.13	
Zr	<.01		<.01		.16	
Co	.057		---		---	
Cr	.051		---		---	
B	Not detected		<.005		<.003	
O ₂	.19		.007		.18	
N ₂	.005		.014		.021	
H ₂	---		.0031		.012	
Formula	$(\text{Ta}_{0.988}\text{Nb}_{0.011}\text{W}_{0.001})\text{C}_{0.932}$	$\text{TaC}_{1.0}$	$\text{HfC}_{0.982}$	$\text{HfC}_{1.0}$	$(\text{Ta}_{0.782}\text{Hf}_{0.202}\text{Nb}_{0.007}\text{Ti}_{0.005}\text{Zr}_{0.004})\text{C}_{0.925}$	$(\text{Hf}_{0.2}\text{Ta}_{0.8})\text{C}_{1.0}$
C, atomic percent	48.2	50	49.6	50	47.9	50
C-metal ratio	0.932	1.0	0.982	1.0	0.925	1.0
Lattice parameter, Å	4.455 (± 0.001)		4.6400 (± 0.0002)		4.493 (± 0.001)	

^aCompositions are single-phase face-centered-cubic materials.

ferred to as $\text{HfC}_{0.98}$. The $(\text{Ta}_{0.782}\text{Hf}_{0.202}\text{Nb}_{0.007}\text{Ti}_{0.005}\text{Zr}_{0.004})\text{C}_{0.925}$ will be referred to either as nominally 80 mole percent $\text{TaC}_{0.93}$ • 20 mole percent $\text{HfC}_{0.93}$ or 80 • 20 composition.

The carbon-metal ratios of the tantalum and hafnium carbides determined from the chemical analysis are 0.93 and 0.98, respectively. The corresponding values obtained through the use of the measured lattice parameters (given in

table I) and published lattice parameters against carbon-metal ratios are 0.95 to 0.99 for tantalum carbide (refs. 10 to 12) and 0.89 to 0.96 for hafnium carbide (refs. 12 to 14). These wide ranges found by use of the various published relations of lattice parameter against carbon-metal ratio are due to difficulty in carbon analysis, variation in kind and content of impurities, and insensitivity of the lattice parameter to carbon content at high carbon concentrations. The carbon-metal ratios determined from the chemical analyses are, however, of the same order of magnitude as those determined from the lattice parameters. The carbon-metal ratio determined by chemical analysis will be used herein because of the insensitivity of lattice parameter to carbon content.

In addition to the three compositions given in table I, compositions of 50 mole percent $\text{TaC}_{0.96}$ · 50 mole percent $\text{HfC}_{0.96}$ and 25 mole percent $\text{TaC}_{0.97}$ · 75 mole percent $\text{HfC}_{0.97}$ were also prepared by mixing $\text{TaC}_{0.93}$ and $\text{HfC}_{0.98}$ powders in the proper ratio before forming the test specimens. The initial carbon-metal ratios given for these compositions after forming were calculated from those of the starting carbides.

Solid cylindrical pieces were formed by hot-pressing at temperatures of 2500° to 3000° K at 3500 pounds per square inch and for times of 10 minutes to 1 hour in a graphite die. Solid cylinders $5/8$ inch in diameter by $1/4$ inch long were formed. The hot-pressing equipment has been described in reference 15. In order to attain homogeneous solid solutions in the 50 · 50 and 25 · 75 specimens, it was necessary to press for 1 hour at 3000° K.

Test specimens $5/8$ inch (O.D.) by $3/8$ inch (I.D.) by $1/4$ inch long were fabricated from the solid hot-pressed cylinders by electric-discharge machining. This hollow-cylinder geometry was used to prevent cracking of the specimen during heating and cooling and for greater uniformity of temperature within those specimens heated directly by induction. An approximate blackbody hole with a depth to diameter ratio of at least 5 to 1 was drilled in the center of the ring parallel to its length. Free carbon was removed from the specimen surface with a wire brush and by grinding manually on 600 abrasive cloth. The homogeneity of the test specimens was judged from the X-ray diffraction patterns.

X-ray diffraction patterns were obtained with a diffractometer at a scanning speed of $1/2^{\circ}$ ($2\theta/\text{min}$) and nickel filtered copper radiation. The lattice parameter values were obtained by applying a least-squares extrapolation of $1/\sin^2\theta$ on an IBM 704 computer.

The densities of the hot-pressed specimens were determined by weighing in air and distilled water on an analytical balance. The theoretical density of each composition was calculated from the measured lattice parameter. The results are expressed as percent of theoretical density. Specimens of 90 to 93 percent of theoretical density were obtained for $\text{TaC}_{0.93}$, 86.6 to 98 percent of theoretical density for 80 · 20 composition, 88.8 to 95.5 percent of theoretical density for 50 · 50 composition, 91 percent of theoretical density for 25 · 75 composition, and 65.5 to 90 percent of theoretical density for $\text{HfC}_{0.98}$.

Vaporization Measurements

The vaporization-rate measurements were carried out in both hot- and cold-wall furnaces to determine the influence of the condensation of the vaporized material on the vaporization rate. The cold-wall furnace has been described in reference 16. In brief, it consists of a 1 inch (I.D.) water-cooled continuously evacuated quartz tube. The specimen was supported on three 0.060-inch-diameter tungsten rods. The specimen was directly heated inductively by a 1/2-megacycle power source. By this arrangement, the hot specimen was directly exposed to the water-cooled quartz tube. A few measurements were also made in a hot-wall furnace, which is described in reference 17. This furnace was also continuously evacuated. The specimen was placed inside a 1-inch-diameter by 1-inch-long tungsten cup, which, in turn, was placed inside a $1\frac{1}{2}$ -inch-diameter by 3-inch-long tungsten susceptor. The susceptor was inductively heated by a low-frequency power source. By this arrangement, the specimen and the walls of the tungsten cup were at approximately the same temperature. There was never any detectable physical adherence of the specimen to the tungsten cup.

The temperature in a sight hole in the specimen was measured with a disappearing-filament optical pyrometer, which had been calibrated against a standard tungsten filament lamp with all optical elements in the light path.

A typical vaporization-rate determination involved weighing the specimen to the nearest 0.2 milligram, inserting the specimen into the furnace, and evacuating the furnace to 1×10^{-6} torr (cold cathode gage). The specimen was then heated slowly to 2100° K so that the pressure never exceeded 1×10^{-4} torr. The time required was about 5 minutes. This temperature was maintained until the system pumped down to less than 5×10^{-5} torr, which required 1 to 2 minutes. The specimen was then brought to the desired temperature in 1 to 2 minutes and maintained constant, $\pm 30^{\circ}$ K, for 1/2 to 1 hour at higher temperatures (2800° to 3000° K) and 2 to 4 hours at lower temperatures (2500° to 2800° K). The pressure during this period was between 5×10^{-5} and 5×10^{-6} torr. At the end of the heating period, the power to the furnace was turned off, and the specimen was cooled to less than 1300° K in 2 minutes. After cooling to room temperature, the specimen was reweighed. The first two determinations on each specimen were made at 2400° to 2500° K. The vaporization rate calculated for the first determination was always very large due to outgassing of highly volatile impurities and was therefore discarded. After the first two determinations, each succeeding measurement was made at a higher temperature. The total heating time for a specimen varied in accordance with the number of measurements made but was always less than 20 hours. The total weight loss of any specimen, even after many determinations, was never greater than 0.5 weight percent. A few preliminary measurements were made at constant temperature with varying heating times. The same general procedure as described previously was followed for these determinations.

The vaporization rate R was calculated from the equation

$$R = \frac{\Delta W}{(\Sigma A)t} \frac{g}{(\text{sq cm})(\text{sec})}$$

where ΔW is the weight lost in grams, t is the time of heating in seconds, and ΣA is the total surface area in square centimeters, which includes the outer cylindrical surface, end surfaces, and "effective" area of the inside of the hollow cylinder. The effective area of the inside of these hollow cylinders was calculated from an equation given in reference 18:

$$A_{ID} = \pi l \left[(d^2 + l^2)^{1/2} - l \right]$$

where l is the length of the cylinder and d is the inside diameter. This expression was derived from the cosine law of vaporization. It corrects for material vaporized from the inside of a hollow cylinder but not lost from the cylinder as a result of recombination on the opposite inner wall. It assumes 100 percent recombination of all material striking the opposite wall. This correction was always less than 10 percent of the total surface area.

RESULTS AND DISCUSSION

The term vaporization is used herein in its broadest sense, that is, to mean a gross mass loss of the specimen. The experimental conditions do not fulfill, in the strictest sense, all the requirements of an ideal Langmuir determination (very large vacuum chamber compared with specimen size, specimen geometry, etc.). The approximations are good enough, however, so that the data may be interpreted as having some kinetic significance.

In this discussion, no extensive reference to kinetics will be made. Also, while it is known that TaC vaporizes incongruently (ref. 5) and HfC congruently (ref. 4), the nature of the vaporization mechanism of the solid solutions is not known, and no conclusions concerning this mechanism are to be drawn from the present data.

X-ray diffraction of the surface of all five hot-pressed compositions, prior to vaporization determinations, showed them to be homogeneous and single-phase face-centered-cubic materials. The lattice parameters of the hot-pressed specimens are shown in the following table. The larger standard deviations for the 50·50 and 25·75 compositions are due to the broader diffraction peaks and lack of resolution of the α_1 , α_2 lines.

Composition, mole percent	Lattice parameter, A
TaC _{0.93}	4.4559 (±0.0006)
80 TaC _{0.93} · 20 HfC _{0.93}	4.4820 (±0.0002)
50 TaC _{0.96} · 50 HfC _{0.96}	4.552 (±0.005)
25 TaC _{0.97} · 75 HfC _{0.97}	4.590 (±0.008)
HfC _{0.98}	4.6400 (±0.0002)

The TaC_{0.93} and 80·20 specimens, in the as-hot-pressed state, were golden yellow, while the other three compositions of higher hafnium content were a silvery gray. After several vaporization determinations, the surface of all compositions was a metallic silver color. The interior of the TaC_{0.93} and 80·20

specimens, even after large weight losses, remained golden yellow. It was observed in the Ta-C system that TaC_x was golden yellow when x was greater than 0.8 and a metallic silver color at less than 0.8 (ref. 19). Evidence was presented that the color transition is related to the electronic structure, which is altered by addition or removal of carbon atoms. For the Ta-C system, the number of electrons per unit cell is decreased by reducing the total number of carbon atoms. In the binary TaC-HfC system, the number of electrons per unit cell is decreased by substituting hafnium for tantalum atoms. This decrease is due to the fact that the hafnium has four electrons in its outer shell, while tantalum has five electrons. Thus, the transition of color caused by either the reduction in carbon content or by hafnium substitution for tantalum can be related to the electron concentration in the unit cell. Therefore, the color change from golden yellow to gray observed in the hot-pressed binary-carbide compositions as the hafnium content increases from $TaC_{0.93}$ to the 50:50 composition is attributed to a decrease in electron concentration. Furthermore, the appearance of a gray surface layer on the initially golden yellow $TaC_{0.93}$ and 80:20 compositions after vaporization measurements is related to a decrease in electron concentration caused by loss of carbon.

The vaporization data for each carbide composition studied is presented individually in figures 1 to 5. Initially, the experimental data points were plotted in these figures and the limits of scatter, indicated by dashed lines, were drawn by inspection to include all the data points. In any figure, for example, figure 2, there is no apparent grouping of any one set of data points

(i.e., one density and furnace condition). This general dispersion of the data points for various sample densities and furnace conditions suggests that, within the range of densities studied and for the two furnace conditions used here, these variables have no significant effect on the measured vaporization rate. The presence or absence of a hot or cold wall had a negligible effect on the vaporization rate of niobium carbide (ref. 20). As a result of this observation, a least-squares line was calculated for each material with all the data points. This least-squares line, shown in figures 1 to 5 as a solid line, was calculated on an IBM 704 computer. In every case, the determination coefficient was greater than 90 percent. This coefficient is the percent probability that there is a linear correlation between the variables, the logarithmic rate, and the reciprocal temperature in $^{\circ}K$.

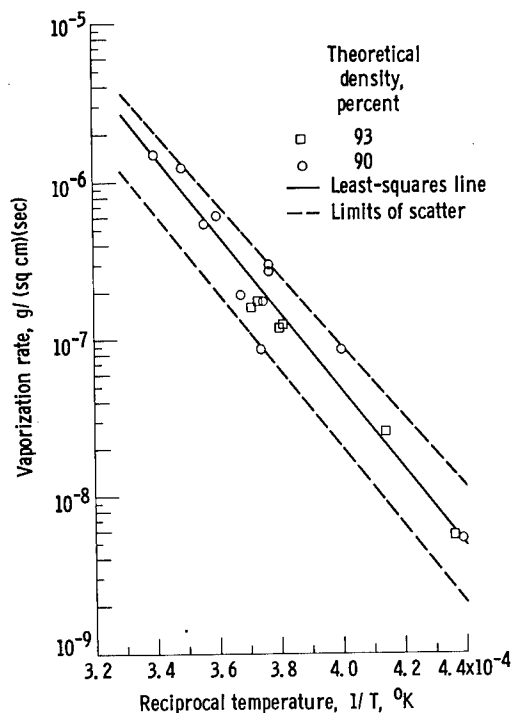


Figure 1. - Vaporization rate of $TaC_{0.93}$ in vacuum in cold-wall furnace as function of temperature.

The vaporization data for $TaC_{0.93}$ specimens of 90 and 93 percent of theoretical density are shown in figure 1. These values were obtained from measurements made in the cold-wall furnace. The vaporization-rate-

data points given in reference 5 for specimens of $\text{TaC}_{0.97}$ with initial densities of 95 percent of theoretical density and in reference 6 for $\text{TaC}_{0.96}$ all fall within the scatter band shown in figure 1. The slopes of the least-squares lines fitted to data points (of refs. 5 and 6) are very nearly equal to one another but approximately 18 percent larger than those obtained from the present measurements. It is suggested that the larger slope for the literature data is due to the difference in the carbon-metal ratios of the specimens (0.93 for the present material compared with 0.96 and 0.97 for the literature carbides).

Vaporization results for the 80 · 20 composition given in figure 2 also show a scatter band. There is some indication that the scatter is less at the higher temperatures.

The vaporization results for the 50 · 50 composition are given in figure 3.

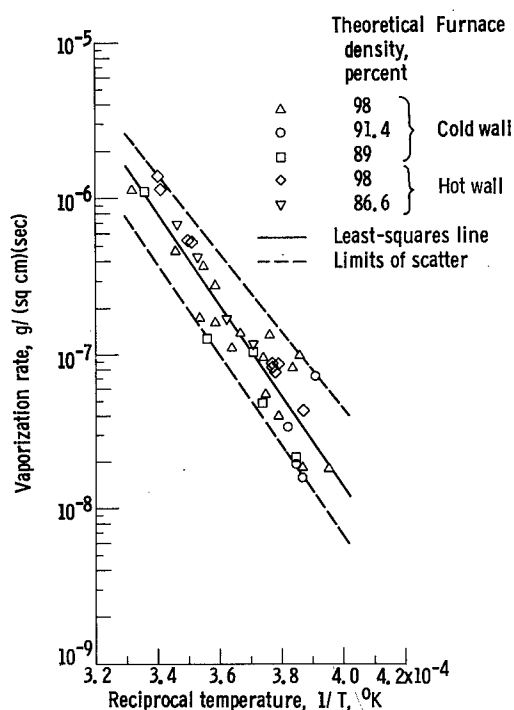


Figure 2. - Vaporization rate of 80 mole percent $\text{TaC}_{0.93}$ · 20 mole percent $\text{HfC}_{0.93}$ in vacuum in cold-wall and hot-wall furnaces as function of temperature.

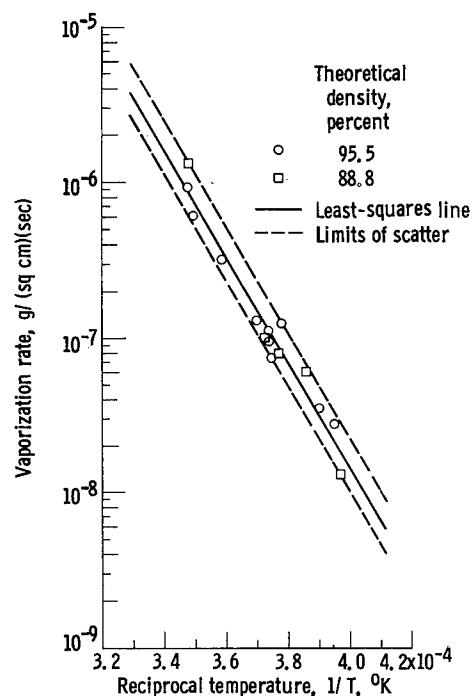


Figure 3. - Vaporization rate of 50 mole percent $\text{TaC}_{0.96}$ · 50 mole percent $\text{HfC}_{0.96}$ in vacuum in cold-wall furnace as function of temperature.

The scatter remains about the same at all temperatures. The vaporization rate of only one specimen of the 25 · 75 composition was measured, and the results are given in figure 4.

The vaporization rate results for $\text{HfC}_{0.98}$ are shown in figure 5. The vaporization-rate-data points given in reference 4 obtained from specimens of $(\text{Hf}_{0.95}\text{Zr}_{0.05})\text{C}_{0.96}$ with an initial density of 70 percent of theoretical den-

sity all fall within the scatter band shown in figure 5. A least-squares fit of the data of reference 4 gives a line with a slope 7-percent greater than

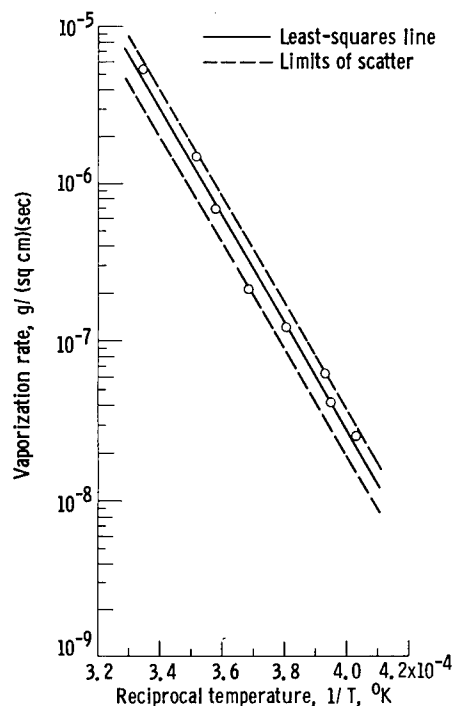


Figure 4. - Vaporization rate of 25 mole percent $\text{TaC}_{0.97} \cdot 75$ mole percent $\text{HfC}_{0.97}$ in vacuum in cold-wall furnace as function of temperature. Initial density of specimen, 91 percent of theoretical density.

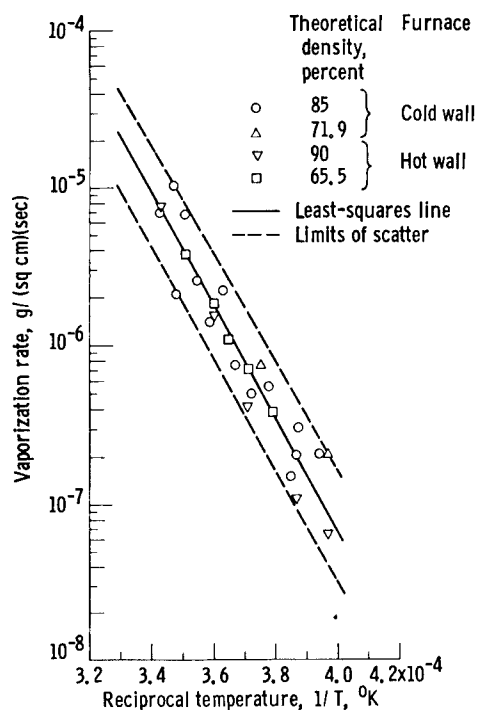


Figure 5. - Vaporization rate of $\text{HfC}_{0.98}$ in vacuum in hot-wall and cold-wall furnaces as function of temperature.

that obtained from the present data. The vaporization-rate data of reference 7 for HfC_x are approximately two orders of magnitude larger than the present data. The slope of the data of reference 7 is almost identical to that given in reference 4. Some of the data of reference 7 for vaporization of other materials was compared (ref. 21) with currently accepted values for these materials; the results of reference 7 were found to be very much larger in every case.

In figure 6, the least-squares-fitted vaporization curves for each carbide composition studied are shown along with data for tungsten. In the case of tungsten the curve represents the literature data (ref. 22), and the points indicate the present determination. The data for tungsten are included so that direct comparisons of the vaporization of the carbides with this material can be made. Tungsten was chosen for comparison because it has the lowest vaporization rate of any known material in this temperature range (2500° to 3000° K). Of the carbide materials studied, the 80 · 20 composition possesses the lowest volatility, and $\text{HfC}_{0.98}$ is the most volatile in the temperature range considered. The vaporization of the 80 · 20 composition approaches that of tungsten at the higher temperatures.

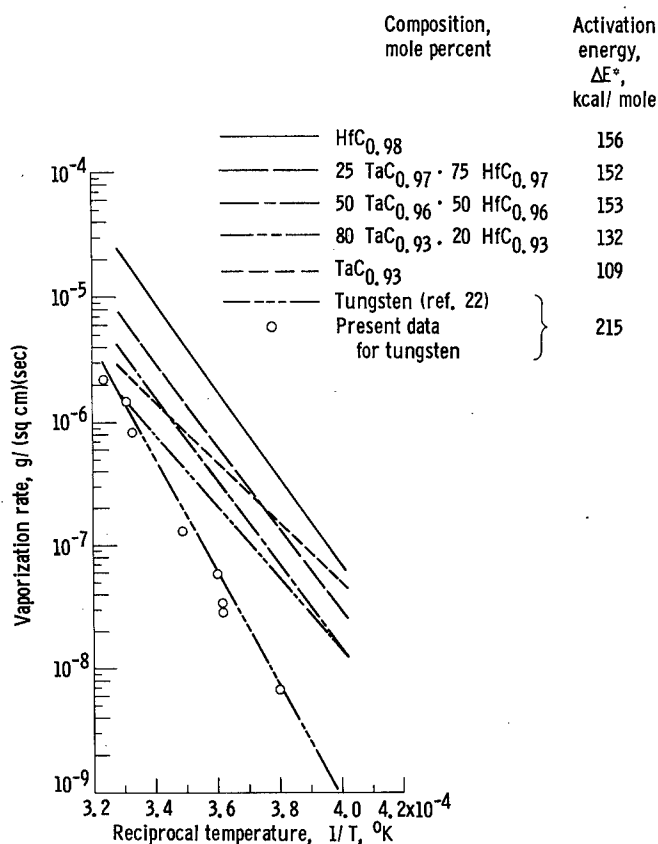


Figure 6. - Comparison of carbide and tungsten vaporization rates in vacuum as function of temperature (least-square lines).

From the slope of the curves for $1/T$ against vaporization rate in figure 6, the activation energy ΔE^* of the vaporization process was calculated from the Arrhenius equation. These values are tabulated in figure 6. Examination of the activation-energy values shows that increasing the TaC content in the binary compositions causes only a slight decrease in ΔE^* up to 50 mole percent TaC. When the TaC content exceeds 50 mole percent, ΔE^* decreases sharply. This suggests that the vaporization processes may be different.

Variation of the vaporization rate as a function of composition at 2500°, 2600°, 2700°, and 2900° K is shown in figure 7. This figure was constructed from the data given in figures 1 to 5. The width of the scatter band and the least-squares vaporization-rate value (shown as a circle) are presented. Straight lines are drawn to pass as near as possible to the least-squares points. It appears that there is a composition near the intersection of these two curves possessing a minimum vaporization rate. This composition lies between the 80 TaC_{0.93} · 20 HfC_{0.93} and 50 TaC_{0.96} · 50 HfC_{0.96} experimental points and is nearer the former.

There are several important points to be made concerning the interpretation of figure 7. The carbon-metal ratio of the experimental materials is not

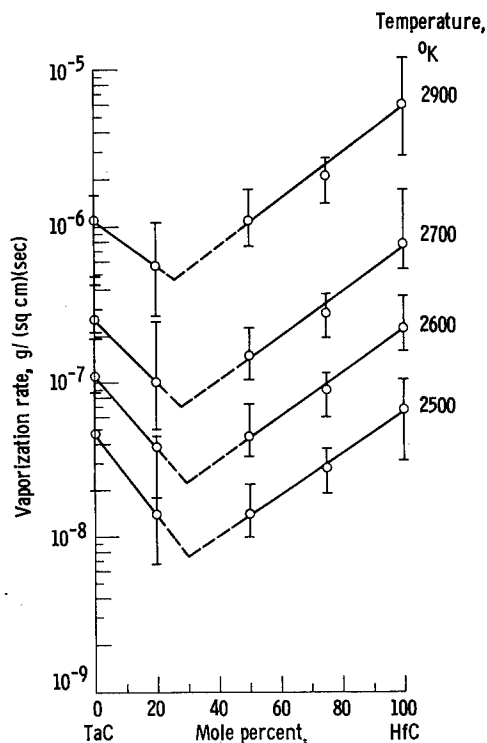


Figure 7. - Vaporization rate in vacuum as function of carbide composition at various temperatures.

constant, but varies from 0.93 for the TaC and 80 · 20 compositions to 0.96 to 0.98 for the 50 · 50, 25 · 75, and HfC compositions, respectively. The vaporization rate for TaC decreases with decreasing carbon-metal ratio (ref. 23). One might therefore similarly argue that the decrease in vaporization rate shown in figure 7 is due to a varying carbon-metal ratio rather than to the TaC to HfC compositional ratio. This is not believed to be true for the following reasons. First, the carbon-metal ratio of the TaC_{0.93} and 80 · 20 compositions are equal; therefore, the observed lower vaporization rate of the 80 · 20 composition, at a given temperature, must be due to the change in the tantalum to hafnium ratio. Secondly, the compositions 50 TaC_{0.96} · 50 HfC_{0.96}, 25 TaC_{0.97} · 75 HfC_{0.97}, and HfC_{0.98} exhibit, for all practical purposes, equal carbon-metal ratios; therefore, the observed decrease in the vaporization rate must also be due to the variation in the tantalum to hafnium ratio in these compositions. Thirdly, from the data of reference 23 for TaC, an estimate of the magnitude and direction of shift of the vaporization rate of the TaC_{0.93} composition at 2700° K could be made if the carbon-metal ratio were raised to a level comparable to the higher carbon content compositions, that is, 0.97. The vaporization rate would be shifted upward from the present 2.5×10^{-7} to about 6×10^{-7} gram per square centimeter per second. For the assumption that the data of reference 23 for TaC also holds for the 80 · 20 composition, an increase in the carbon-metal ratio to 0.97 would shift the vaporization rate of this material upward from 1×10^{-7} to about 3.5×10^{-7} gram per square centimeter per second. This would shift the composition of the minimum toward higher hafnium contents (i.e., from about 30 up to approx. 50 mole percent HfC). This would not, however, negate the basic conclusion that a composition exists in the TaC_x-HfC_x binary system, which possesses a minimum volatility.

Another factor that could influence this conclusion is the effect of heating time on the vaporization-rate values. Preliminary data (from a continuing program) for TaC_{0.93} and the 80 · 20 composition at 2600° K, in the cold-wall furnace, show that the vaporization rate decreases with increased heating time. The vaporization rate of TaC_{0.93} decreases from 1×10^{-7} to 7×10^{-8} gram per square centimeter per second in 13 hours, while the 80 · 20 composition shows a decrease from 4×10^{-8} to 2×10^{-8} gram per square centimeter per second in 40 hours. In both cases, the new values are within the scatter band of the short-time data reported herein. Furthermore, the heating time used for a rate determination at a given temperature for each composition was approximately the same. This then further minimizes the effect of time on the vaporization-rate values and, from the standpoint of the time effect, makes the compositional comparison of figure 7 valid at a given temperature.

Kaufman and Stepakoff (ref. 24) applied the Schottky-Wagner model to the ternary Ta-Hf-C system and calculated the vapor pressures of Ta, Hf, and C over (Ta-Hf)C as a function of temperature and composition. From these values, they calculated the vaporization rates through the Langmuir equation. The calculated initial rates of vaporization from reference 24 show fair agreement with observed rates at 2600° K. Also, the observed minimum in the vaporization rate is predicted from the calculations given in reference 24.

CONCLUDING REMARKS

All evidence indicates that there is a composition in the binary system between TaC_x and HfC_x that possesses a minimum volatility or a maximum stability. This composition appears to be near the 80 mole percent $TaC_{0.93}$ · 20 mole percent $HfC_{0.93}$ experimental composition. The vaporization rate of this composition approaches that of tungsten at high temperatures. The influence of density variation and vapor-specie condensation of the vaporization rate is less than the precision of measurement of the vaporization rate. With the passage of time, at a constant temperature, the vaporization rate of both $TaC_{0.93}$ and the 80 mole percent $TaC_{0.93}$ · 20 mole percent $HfC_{0.93}$ compositions decreased. This decrease is not large and is well within the scatter band in each case.

Lewis Research Center

National Aeronautics and Space Administration

Cleveland, Ohio, May 11, 1964

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NASA TN D-2512
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(NASA TECHNICAL NOTE D-2512)

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